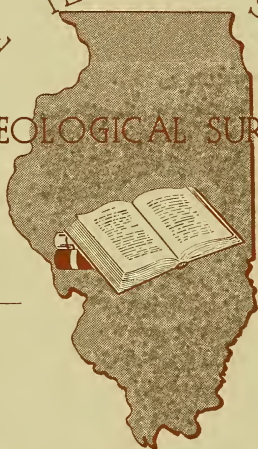




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RECENT WORK ON SILICATE AND RELATED  
SYSTEMS INVOLVING CHEMICAL  
COMPONENTS OF ILLINOIS  
SEDIMENTARY ROCKS

BY  
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## Recent Work on Silicate and Related Systems Involving Chemical Components of Illinois Sedimentary Rocks\*

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### INTRODUCTION

The taking from the earth of various materials and the utilization of them, either directly or indirectly, in the production of socially useful objects, is as old as man himself. As milestones in this development might be mentioned the construction of caves and mud shelters for habitation. Later, with the discovery of fire, came the burning of crude clay wares both for structural and artistic purposes, and the production of crude glass. Out of these humble beginnings studies of the relationships between chemical composition of materials taken from the earth, temperature, and properties of the finished product have been slowly developing through their empirical stage and are in the present gaining a truly scientific foothold in the accumulated experience of civilization. Today we have better cements, glass, refractories, bricks, insulation materials, steel, and better building materials in general chiefly because we understand these relationships more thoroughly. In the present paper it is desired to present in necessarily brief form, considering the immensity of the subject, a glimpse of the state of high-temperature research on silicate and related systems.

### The Basis of Recent Advances

Advances in high temperature silicate chemistry are the result of a combination of developments both on the theoretical and practical side. Of great significance on the theoretical side has been the phase rule of Willard Gibbs, the theorem of Le Chatelier and its quantitative expression in the form of the Clausius Clapeyron equation. Practically, recent advances in the fields of high temperature furnaces, thermoelectric pyrometry, microscopy, and the development of the quenching method and other techniques by the Geophysical Laboratory in Washington have been of major importance. The general impetus given work in the field of high temperature silicate chemistry by this latter institution both in the development of new techniques and apparatus, and in performing a tremendous amount of experimental research is deserving of the highest praise.

Experimentally, data for the construction of diagrams illustrating phase relationships at equilibrium are obtained by holding intimate mixtures, of definite composition, expressible in terms of the components of the system investigated, at a definite temperature, allowing the system to come to equilibrium and determining the relative amounts and the nature of the phases present under these conditions.

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### The Body of Experimental Data

Upon examination of the average composition of the lithosphere<sup>1</sup> it is of little wonder that the greater part of researches on silicate and related systems have dealt with those systems the composition of which can be expressed by some combination of the oxides,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  in varying proportions. On the calcined, or  $\text{CO}_2$  and  $\text{H}_2\text{O}$  free basis, roughly 98 per cent of both igneous and sedimentary rocks is represented by these oxides. Consider further the position of these materials in industry. Ordinary portland cement, cements containing granulated blast furnace slag, pozzolanas and pozzolanic cement, and aluminous cement can all be represented in systems of components chosen chiefly from the above oxides. Likewise is this true of ordinary glass, silica, dolomite and fireclay refractories, bricks, tile, whiteware, porcelain, rock, slag and glass wool. Were we to imagine our present civilization minus cement, steel and glass, as we now know them, the importance of scientific information on systems composed of these oxides becomes strikingly apparent.

Although a detailed analysis of any of the individual systems studied cannot be given, the type of information procured in the field of research on silicate and related systems has to do, in the majority of cases, with the relationship of composition and temperature to the formation of compounds, eutectics, solid solutions, immiscible liquids, fields of stable phases, the distribution of phases, and to the physical properties of certain products derived from the systems. Tables I, II and III illustrate silicate and related systems on which work of this nature has in some degree been performed. One of the most pleasing phases of this work is the wide applicability of results to any problems involving the components of the particular system studied, i.e., its fundamental character. Thus the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system has been helpful in problems not only in the cement industry, but in problems of the metallurgical and ceramic fields as well. Indeed, much of the work on phase equilibria performed by the Geophysical Laboratory in Washington, primarily concerned with geological application, has contributed equally as much in the industrial field.

This body of information is related fundamentally to the utilization of Illinois sedimentary rocks: In the first place the compositions of Illinois rocks can be expressed almost solely in terms of the oxides previously shown to be the major components in systems including the majority of products in the cement and ceramic industries, and the major components in metallurgical slags; as a matter of fact, a considerable Illinois production is utilized by these industries. Secondly, the complete phase equilibrium data of, and the properties of the various materials occurring within systems formed from the components in the sedimentary rocks are not fully known. These facts have been instrumental in developing the viewpoint on the part of the Illinois State Geological Survey that certain carefully selected avenues of research might contribute valuable information in the field of non-fuels technology in the State, both in the creation of new products and the improvement of old. The third point looks into the future a considerable distance, perhaps. A mixture of silicates in the molten state when allowed to cool delivers crystalline materials from solution, not haphazardly, but in an ordered manner predictable from phase equilibrium data. This suggests the possibility of extracting, by fractional crystallization from a cooling melt, pure minerals to be used, after cooling and grinding, as such, or in combination with other materials for the synthesis of new products. Likewise can be visualized a "silicate alloy" industry, preparing silicate glasses of desired composition and grain size to be utilized as the glassy bonding materials in ceramic wares.

Silicate Systems

Completely or partially studied by various investigators from a standpoint of phase equilibrium relationships and other properties. These studies were made at relatively high temperatures in all but a few cases.

TABLE I

SiO <sub>2</sub>			
Binary	Ternary		
Al <sub>2</sub> O <sub>3</sub>	CaO Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O Fe <sub>2</sub> O <sub>3</sub>	Quaternary
CaO	MgO	MgO	
MgO	FeO	K <sub>2</sub> SiO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> —Fe <sub>2</sub> O <sub>3</sub>
FeO	Fe <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub> —Na <sub>2</sub> O
Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	ZrO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub> —Na <sub>2</sub> O
Na <sub>2</sub> O	K <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	FeO—Fe <sub>2</sub> O <sub>3</sub>
K <sub>2</sub> O.SiO <sub>2</sub>	CaF <sub>2</sub>	CO <sub>2</sub>	MgO—FeO
MnO	BaO	H <sub>2</sub> O	TiO <sub>2</sub> —MgO
PbO	SrO	NaF	TiO <sub>2</sub> —MnO
CaO.SiO <sub>2</sub>	TiO <sub>2</sub>	Na <sub>2</sub> O.SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> —FeO—Fe <sub>2</sub> O <sub>3</sub>
Na <sub>2</sub> O.SiO <sub>2</sub>	Li <sub>2</sub> O	CaO.SiO <sub>2</sub>	K <sub>2</sub> O—Na <sub>2</sub> O
K <sub>2</sub> CO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO—TiO <sub>2</sub>
Na <sub>3</sub> AlF <sub>6</sub>	CO <sub>2</sub>	K <sub>2</sub> O PbO	CaO—K <sub>2</sub> O
SrO	H <sub>2</sub> O	MgO	Na <sub>2</sub> O—FeO
BaO	MnO	CO <sub>2</sub>	K <sub>2</sub> O—Fe <sub>2</sub> O <sub>3</sub>
Li <sub>2</sub> O	B <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	
CaS	—Al <sub>2</sub> O <sub>3</sub> MgO	FeO MgO	
Pb <sub>3</sub> O <sub>4</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	
ZnO	Fe <sub>2</sub> O <sub>3</sub>	SnO	
B <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MnO	
SnO	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>  ZnO	
ZrO <sub>2</sub>	Na <sub>3</sub> AlF <sub>6</sub>	MnO TiO <sub>2</sub>	
TiO <sub>2</sub>	TiO <sub>2</sub>	Pb <sub>3</sub> O <sub>4</sub>  K <sub>2</sub> CO <sub>3</sub>	
BeO	Li <sub>2</sub> O	CuO V <sub>2</sub> O <sub>5</sub>	
Cr <sub>2</sub> O <sub>3</sub>	MnO	Al S	
MnS	BaO	Fe S	
MnO	ZnO		
	H <sub>2</sub> O		

Systems of more than four components:

- SiO<sub>2</sub>—CaO—Al<sub>2</sub>O<sub>3</sub>—MgO—Na<sub>2</sub>O
- SiO<sub>2</sub>—CaO—Al<sub>2</sub>O<sub>3</sub>—MgO—K<sub>2</sub>O
- SiO<sub>2</sub>—CaO—Al<sub>2</sub>O<sub>3</sub>—MgO—Na<sub>2</sub>O—Fe<sub>2</sub>O<sub>3</sub>—FeO
- SiO<sub>2</sub>—Si—MnO—Mn—FeO—Fe

TABLE II  
Systems Without SiO<sub>2</sub>

CaO MgO	Al <sub>2</sub> O <sub>3</sub>  MgO	CaO Al <sub>2</sub> O <sub>3</sub> —K <sub>2</sub> O
Al <sub>2</sub> O <sub>3</sub>	CaF <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub> —Na <sub>2</sub> O
Fe <sub>2</sub> O <sub>3</sub>	ZnO	Al <sub>2</sub> O <sub>3</sub> —MgO
B <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> —Fe <sub>2</sub> O <sub>3</sub>
ZrO <sub>2</sub>	TiO <sub>2</sub>	NaF CaF <sub>2</sub> —AlF <sub>3</sub>
NaF AlF <sub>3</sub>	ZrO <sub>2</sub>  ThO <sub>2</sub>	MgO FeO—Fe <sub>2</sub> O <sub>3</sub>
KF	PbO	Fe <sub>2</sub> O <sub>3</sub>  Fe <sub>3</sub> O <sub>4</sub> —O <sub>2</sub>
CaF <sub>2</sub>	PbF <sub>2</sub>	Na <sub>2</sub> O K <sub>2</sub> O—B <sub>2</sub> O <sub>3</sub>
PbF <sub>2</sub>	Bi <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O—As <sub>2</sub> O <sub>5</sub>
CdF <sub>2</sub>	As <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O—Cr <sub>2</sub> O <sub>3</sub>
AlF <sub>3</sub>  KF	V <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O—WO <sub>3</sub>
LiF	MoO <sub>3</sub>	K <sub>2</sub> O—MoO <sub>3</sub>
MgF <sub>2</sub>  LiF	CrO <sub>3</sub>	MoO <sub>3</sub> —WO <sub>3</sub>
CaF <sub>2</sub>	WO <sub>3</sub>	PbO CrO <sub>3</sub> —SO <sub>3</sub>
KF BaF <sub>2</sub>	FeO MgO	MoO <sub>3</sub> —WO <sub>3</sub>
B <sub>2</sub> O <sub>3</sub>  Li <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	MoO <sub>3</sub> —Bi <sub>2</sub> O <sub>3</sub>
Na <sub>2</sub> O	Na <sub>2</sub> O TiO <sub>2</sub>	WO <sub>3</sub> —Bi <sub>2</sub> O <sub>3</sub>
CdO	As <sub>2</sub> O <sub>5</sub>	PbF <sub>2</sub> —As <sub>2</sub> O <sub>5</sub>
MnO	MoO <sub>3</sub>	PbF <sub>2</sub> —V <sub>2</sub> O <sub>5</sub>
PbO	WO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>  NaF—AlF <sub>3</sub>
	K <sub>2</sub> O As <sub>2</sub> O <sub>5</sub>	NaF—AlF <sub>3</sub> —CaF <sub>2</sub>
	MoO <sub>3</sub>	
	WO <sub>3</sub>	
	TiO <sub>2</sub>  ThO <sub>2</sub>	

TABLE III  
*Melting Diagrams*

MgO	NiO	Al <sub>2</sub> O <sub>3</sub>	CaO	ZrO <sub>2</sub>	CaO	ZrO <sub>2</sub>	CeO <sub>2</sub> —Ce <sub>2</sub> O <sub>3</sub>
	CoO		BaO		SrO		BeO—CaO
	Al <sub>2</sub> O <sub>3</sub>		SrO		BaO		BeO—CeO <sub>2</sub>
	Cr <sub>2</sub> O <sub>3</sub>		MgO		BeO		ThO <sub>2</sub> —CaO
	Fe <sub>3</sub> O <sub>4</sub>		NiO		MgO		ThO <sub>2</sub> —MgO
	Mn <sub>3</sub> O <sub>4</sub>		CoO		ZnO		
	SiO <sub>2</sub>		TiO <sub>2</sub>		NiO		BeO
	TiO <sub>2</sub>		SiO <sub>2</sub>		CoO		CaO
	ZrO <sub>2</sub>		BeO		Al <sub>2</sub> O <sub>3</sub>		CeO <sub>2</sub>
	Cu <sub>2</sub> O		Cu <sub>2</sub> O		Cr <sub>2</sub> O <sub>3</sub>		CoO
	CaO		ZrO <sub>2</sub>		Fe <sub>2</sub> O <sub>3</sub>		Cr <sub>2</sub> O <sub>3</sub>
	BaO		ThO <sub>2</sub>		Mn <sub>3</sub> O <sub>4</sub>		Cu <sub>2</sub> O
	SrO		CeO <sub>2</sub>		La <sub>2</sub> O <sub>3</sub>		Fe <sub>3</sub> O <sub>4</sub>
	BeO		La <sub>2</sub> O <sub>3</sub>				La <sub>2</sub> O <sub>3</sub>
	CeO <sub>2</sub>		Mn <sub>3</sub> O <sub>4</sub>	CaO	Mn <sub>3</sub> O <sub>4</sub>		Mn <sub>3</sub> O <sub>4</sub>
	La <sub>2</sub> O <sub>3</sub>		Fe <sub>3</sub> O <sub>4</sub>		Cu <sub>2</sub> O		NiO
SiO <sub>2</sub>	K <sub>2</sub> O		Ga <sub>2</sub> O <sub>3</sub>		TiO <sub>2</sub>		ThO <sub>2</sub>
	Rb <sub>2</sub> O		Cr <sub>2</sub> O <sub>3</sub>		CoO		TiO <sub>2</sub>
	Cs <sub>2</sub> O				NiO		
		CeO <sub>2</sub>	CaO		ThO <sub>2</sub>		
			Cr <sub>2</sub> O <sub>3</sub>		Cr <sub>2</sub> O <sub>3</sub>		
			Fe <sub>3</sub> O <sub>4</sub>				
			Mn <sub>3</sub> O <sub>4</sub>				
			ZrO <sub>2</sub>				

### Cone Deformation Diagrams

- $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{CaO}$   
 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{MgO}$   
 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{FeO}$   
 $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 - \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$   
 Microcline—steatite  
 Microcline—albite  
 Orthoclase—CaO  
 Orthoclase—MgO  
 Albite—CaO  
 Albite—MgO  
 Feldspar—Flint—Kaolin

## BIBLIOGRAPHY

1. The Data of Geochemistry: F. W. Clarke U. S. Geological Survey Bulletin 770, p. 34.
2. A Compilation of Phase-Rule Diagrams of Interest to the Ceramist and Silicate Technologist: F. P. Hall and Herbert Insley. Journal of the American Ceramic Society 16, 455-567 (1933).
3. Supplement to A Compilation of Phase-Rule Diagrams of Interest to the Ceramist and Silicate Technologist: F. P. Hall and Herbert Insley. Journal of the American Ceramic Society 21, 113-157 (1938).

Note: Due to lack of space it is impossible to include in the bibliography references to all the systems in the Tables. Systems not referred to in references 2 and 3 above will be gladly furnished by the author.

Since this paper was presented, a good deal of phase equilibrium data has appeared in the literature. The tables have been revised in this paper therefore to include these new systems, most of which are taken from Reference 3.





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